Original Article

Removing Fe, Zn and Mn from steel making plant wastewater using RO and NF membranes

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Abstract

Background and purpose: Excessive amount of heavy metals in industrial wastewater is a seriou crucial issue and requires efficient methods to be introduced and dealt with. Meanwhile, steel mak plants as productive units in every country release large amounts of fluid into surface underground sources. Typically, this wastewater contains heavy metals in minor amounts, while amount could cause severe damages to the living organisms.

Materials and methods: In this study, removing iron, manganese, zinc and total dissolved solid i typical wastewater resulted from steel making plant was considered using reverse osmosis (RO) nanofiltration (NF) membranes. At first, different pH values and operating pressures were applie the wastewater. Then, these parameters were evaluated for a wastewater only containing iron compare the interaction of other elements in iron removal.

Results: The results indicated that RO and NF membranes could successfully treat indust wastewater containing several heavy metals with high concentrations of Fe, Zn and Mn, especiall optimum pH and pressure. Moreover, the interaction of other heavy metals and components in influent decreased the efficiency of RO but improved the NF efficiency to remove iron. To hav better image, a formula was proposed for each method to represent the influence of the parameters removal rates. Finally, cost estimation for both procedures showed that RO was not economica technically efficient in comparison with NF.

Conclusion: NF showed an acceptable performance with high water flow which made it m suitable for industries. At the end, the relative cost analysis showed that even if the initial price of is high, the energy consumption and total cost of RO will be higher.

Key Words: Heavy metals; Environment; Regression; Cost

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1. Introduction

Heavy metals are among elements that exhibit metallic properties and possess specific gravity greater than 5. With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries, pesticides, etc., heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries (1, 2). Some of these heavy metals such as iron, cobalt, copper, manganese and zinc are vital for living organisms while their excessive amounts can be damaging to them. On the other hand, mercury, cadmium and chromium are toxic, and their accumulation over time can cause severe damages to body of living things (3). Typically, iron, zinc and manganese removal is among the problematic issues for making potable water. These three important elements are the major objective of this research (1-3). One industry which may generate high levels of iron, manganese, zinc, cadmium and cyanide in its wastewater is steel making plant. Water as the essential part of steel making process becomes polluted while solving various components and elements. In recent years, due to strict regulations and improved levels of water bodies, necessity of presenting a new method for wastewater treatment resulting from steel making plants seems to be critical. In addition, high volumes of water are required to generate steel products, and an efficient treatment of the resulting wastewater could be the solution for the demanded water. Of course, if the quality of the treated water is appropriate, it may be used as the water necessary for irrigation, sanitary uses, and so on in this plant. Currently, large amounts of water are used in steel making plants. As an example reported that in India, on average, each ton of steel production requires 25 to 60 cubic meters of water and 4 to 5 tons of other raw materials (4). In another case, China was introduced as the largest steel output in the world, and water consumption by iron and steel industry accounted for about 14% of the total industrial water used in China (5). Furthermore, Beh reported that each steel mill in Malaysia used an average of about $18000\ m^3$ of water per day. This large amount of water was mainly used in steel production for cooling purposes (6). These three examples from different parts of the world indicate that steel making is a water-dependent industry in which a practical treatment method can help to save water resources. Although there are several methods such as electro-coagulation, oxidation/filtration, ion-exchange and adsorption to remove heavy metals, there still exists no regular information on iron, manganese and zinc removal using membrane filtration methods. Besides, many of the mentioned methods have some limitations such as rapid clogging and pollutant concentrations (7, 8). Membrane filtration as a new technology is among the methods which are being improved globally due to recent applications of this technology all over the world. Different types of membranes have shown great promise for heavy metal removal for their high efficiency, easy operation and space saving (2). In general, membrane technology is divided into four major methods: Ultra-filtration (UF), Reverse Osmosis (RO), Nanofiltration (NF), and Electro-dialysis (ED). Nanofiltration (NF) is the intermediate process between UF and RO. NF is a promising technology for the rejection of heavy metal ions, such as nickel, chromium, copper, and arsenic from wastewater. NF process benefits from ease of operation, reliability, and comparatively low energy consumption as well as high efficiency of pollutant removal (2, 3). NF membrane could remove Cd, Mn and Pb with 99%, 89% and 74% efficiency (9). On the other hand, the reverse osmosis (RO) process takes advantage of a semi-permeable membrane which allows the purified fluid to pass through it while rejecting the contaminants. RO is an increasingly popular wastewater treatment option in chemical and environmental engineering. Recently, the application of appropriate RO systems to remove heavy metals has also been investigated, but the result was that these metals have yet to be widely applied (2). Mostly copper, nickel, arsenic, zinc and chromium have been removed using RO with normally higher than 95% up to 99.5% efficiency, and no clear result has been achieved for RO in previous studies (2). Separation occurs in NF and RO due to solution diffusion as well as sieving, the Donnan effect, dielectric exclusion, and electro-migration, which make them useful in the separation of both charged and uncharged organic solutes (10). Additionally, the feed pH can change the nature of the membrane surface charge and pore size, as well as that of dissolved metal species, and therefore can affect the membrane separation efficiency (10). Huang used wetland as pretreatment method to remove pollutants from an iron and steel enterprise using ultrafiltration and reverse osmosis methods to remove iron and manganese. As it was reported, the initial concentration of Fe and Mn were 1.59 mg/lit and 0.53 mg/lit, respectively (5). In the other study, Al-Jlil et al. used RO and Saudi bentonite clay as adsorbent to remove heavy metals from a wastewater (Co, As, Co and Cr). The minimum rejection of heavy metals by RO was about 88%, while the minimum rejection by adsorption was about 89% (11). Ultra-filtration and microfiltration is unable to fully eliminate dissolved inorganic constituents such as iron and manganese (3). Because normally ultra-filtration and micro-filtration methods have lower efficiency in comparison with reverse osmosis and nanofiltration, thus RO and NF is applied in this study to remove iron, manganese, zinc, TDS, EC, and turbidity from a steel making plant wastewater. Although previous studies evaluated iron, manganese and zinc rejection (5,11), none of them considered high concentration of these heavy metals applying both RO and NF membranes for a steel making enterprise. The main focus of this research was then to consider high concentrations of iron, manganese and zinc in wastewater influent from a steel making plant. Thus, the performance of two membranes filtration methods namely reverse osmosis and nanofiltration are compared both technically and economically. Mathematical relations are used to have better understanding of both methods.

2. Materials and Methods

2.1. Simulated Wastewater

In this study, simulated wastewater was applied to RO and NF membranes. The characteristics of steel making plant wastewater were obtained from the results of a wastewater in Malaysia. The characteristics of steel making plant wastewater and Standard B values of Malaysia (6).

Table 1. Characteristic of steel making plant

Parameter	Before Treatment (mg/l)	Standard B
pH	6.30	5.50-9.00
Temperature	26.50	40.00
BOD_5	80.40	50.00
COD	361.00	200.00
Total Suspended Solids	345.00	100.00
Cyanide as C_N	N.D. (<0.01)	0.10
Boron as B	0.50	4.00
Phenol	N.D. (<0.001)	1.00
Free Chlorine as Cl_2	N.D. (<0.01)	2.00
Sulphide as S	N.D. (<0.01)	0.50
Oil & Grease	N.D. (<0.5)	10
Cadmium as Cd	N.D. (<0.001)	0.02
Chromium as Cr^{+3}	N.D. (<0.03)	1.00
Chromium as Cr^{+6}	N.D. (<0.005)	0.05
Lead as Pb	N.D. (<0.01)	0.50
Copper as Cu	0.83	1.00
Manganese as Mn	1.56	1.00
Nickel as Ni	N.D. (<0.01)	1.00
Zinc as Zn	4.02	2.00
Iron as Fe	23.30	5.00
Mercury as Hg	N.D. (<0.001)	0.05
Arsenic as As	N.D. (<0.001)	0.10
Tin as Sn	N.D. (<0.002)	1.00
Silver as Ag	N.D. (<0.02)	1.00
Aluminium as Al	1.46	15.00
Fluoride as F	1.44	5.00
Ammoniacal Nitrogen as N	1.35	20.00
Barium as Ba	N.D. (<0.05)	2.00
Formaldehyde	N.D. (<0.2)	2.00

* N.D. means Not Detected

It is notable that the temperature of influent was 26.5℃. As it can be seen from Table 1, iron ($23.3\ mg/L$), zinc ($4.02\ mg/L$), and manganese ($1.56\ mg/L$) have the highest concentrations with iron preceding the other values. According to this table, all other elements meet the standard values except Fe, Mn and Zn. Therefore, if only Fe, Mn and Zn concentrations are observed and treated, no other threat exists for environment. Of course, besides Fe, Zn and Mn, the values of BOD, COD and TSS should be treated to satisfy the standard limitations (6).

2.2 Methodology

The RO and NF tests were performed using thin-film polyamide composite membranes with a spiral wound configuration. The type of RO membrane was a Film-Tec BW30-4040, while NF membrane was a Film-Tec NF90-4040. Table 2 shows the general information about RO and NF membranes.

All chemicals ($CuCl_2.2H_2O$, $MnCl_2.4H_2O$, $Zn(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$, $AlCl_3.6H_2O$, NaF, NH_4NO_3, HCl and NaOH) used in this research were the products of Merck, made in Germany. Conducting the experiments, the influent was stored in a tank ($200\ L$) which passed a 1-micron micro-filtration to remove the total suspended solids (sand, silt, dirt and dust particles). Then, it entered a granular activated carbon cartridge to remove the probable chlorine, taste and odor. A schematic diagram of the laboratory-scale assembly used is shown in Figure 1. All experiments were conducted at constant room temperature 25℃. The volume of storage tank was 50 l ($0.05\ m^3$), and the concentration was adjusted by using a mixer in the tank. Additionally, the concentration and pH were controlled repetitively during the experiment. This experiment was a close system; i.e. one mix was prepared, and the experiments were carried out on the influent.

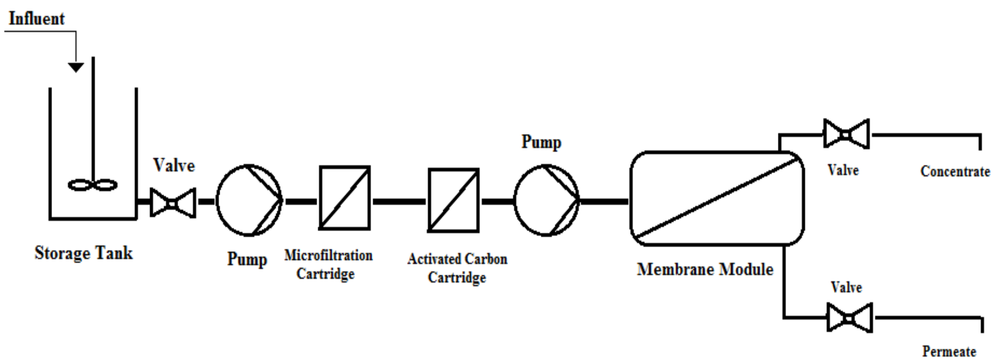

Figure 1. Diagram of laboratory-scale: reverse osmosis and nanofiltration systems

Table 2. Characteristics of Film-Tec membranes

Product	Type	Active Area (m^2)	Maximum Operating Pressure	Maximum Operating Temperature	pH Range	Free Chlorine Tolerance
RO: BW 30-4040	Polyamide Thin Film Composite	7.2	41 bar	45 ℃	2-11	0.1 ppm
NF: NF 90-4040	Polyamide Thin Film Composite	7.6	12 bar	40 ℃	3-11	0.1 ppm

Since ultra-filtration and micro-filtration methods are normally unable to treat heavy metals efficiently, RO and NF was applied in the present study to remove iron, manganese, zinc, TDS and EC from a simulated steel making plant wastewater. In this research, in the first step, the optimum pressure was found, and at this pressure the effect of pH on the iron, manganese and zinc removal (as the highest available concentration in the wastewater), as well as TDS were studied. Meanwhile, for all experiments, the value of permeate flow was reported. Then, at optimum pH and pressure, the Fe concentration (as the highest available concentration) was changed to observe the efficiency of RO and NF membranes in the higher heavy metal concentrations. Finally, to determine the effect of other ions on iron removal, a simulated wastewater containing only Fe was prepared and introduced to RO and NF membranes to compare the iron removal efficiency for both wastewaters. At the end, by comparing the achieved results from both RO and NF membranes, as well as cost comparison of them, the suitable membrane for this steel making plant wastewater would be reported. To have a better understanding of the influence of all parameters on removal rates, formulas would be proposed for each treatment method.

2.3 Applied Relations

Water flux measurements were carried out using Eq. (1) at each constant pressure, where J_v is the permeate flux $(\frac{L}{m^2h})$, A is the effective area (m^2) and Q is the volume flow rate $(\frac{L}{h})$ [10]:

$J_v = Q/A$ *Eq. (1)*

To measure the heavy metal removal, an initial concentration of the heavy metal was added to the reservoir tank and then pumped and agitated through the membrane module. The removal efficiency is stated using Eq. (2) where $E(\%)$ is the removal efficiency and C_p and C_0 are the permeate and feed concentration (12):

$E(\%) = \left[1 - \frac{C_p}{C_0}\right] \times 100$ *Eq. (2)*

The experiments have been done for two influents. I) influent only containing iron called [*WF*] II), and influent containing all elements listed in Table 1, called [*COM*]. The biggest achievement of two different influents is the ability to compare the influence of other components (elements) on iron removal. For RO membrane, experiments were run at different pressures (7, 9, 11 and 13 bar) at constant value $pH = 8$. In this step, the highest rejection as well as the favorable permeate flow rate were found, because by varying the applied pressure, the flow rates changed. Then, at the optimum pressure, pH values varied from 5 to 9.5. As it was previously discussed, the influence of pH is important, because pH changes the nature of the membrane surface charge and pore size. Finally, at optimum pressure and pH, the concentration of Fe varied to observe the capability of RO in high concentration removal. All tests have been performed at a constant temperature of 25℃. All changes in TDS, EC, water flux and concentrations of Fe, Zn and Mn were observed for all variables. For NF membrane, the condition was the same as RO, except the variation of pressure (5, 7, 9 and 11 bar) at constant value $pH = 8$.

2.4. Effect of Operating Pressure

For RO membrane, operating pressure varied from 7 to 13 bar to find the optimum pressure, because a low pressure RO was applied in the current study. Variation of the operating pressure can affect the permeate flow rate as well as the rejection of the solutes (13). The pressure variation was done for all types of influents (containing only Fe [WF] or all components [COM]) to compare the removal efficiency of the parameters. Similarly, the process was repeated for NF membrane, but pressure varied from 5 to 11 bar. The concentration of metal ions was also experimented using a (PC Spectro Lovibond) spectrometer.

2.5. Effect of pH

The pH level was measured using a calibrated pH meter (WTW SERIES, pH 730). Optimum pressure was applied to the influent, and the value of pH was changed from 5 to 9.5 to find the best possible pH for Fe, Mn, Zn, TDS and EC removal. It was previously found that pH affects the separation by its influence on the hydration and absorption capacity of the solutes on the membrane (13). It is notable that pH variation was observed for all types of influents (containing only Fe [WF] or all components [COM]) to compare the removal efficiency of the parameters.

2.6. Effect of Feed Concentration

The concentration of feed water was altered to observe the capability of RO and NF to remove the high concentrations of Fe while other items were kept constant. The main reason for choosing iron concentration is its relative high concentration in the influent in comparison with other elements. At the same time, the feed concentration could affect the permeate flow rate and solute rejection (13).

3. Results

3.1 RO Membrane

As was mentioned above, applied pressure varied from 7 to 13 bar in RO membrane, and pH values varied from 5 to 9.5. Table 3 shows the removal efficiency of Fe, Zn, Mn, TDS and EC for WF and COM wastewaters.

Table 3. Removal efficiency of Fe, Mn, Zn, TDS and EC in RO membrane for different pHs and pressures

Type of Influent		WF	COM	WF	COM	WF	COM	COM
Constant pH=8	**Pressure**	EC $(\mu s/cm)$	EC $(\mu s/cm)$	TDS (mg/L)	TDS (mg/L)	C_{Fe} (mg/L)	C_{Fe} (mg/L)	C_{Zn} & C_{Mn} (mg/L)
	7	88.9%	85.4%	89.3%	85.8%	100.0%	99.5%	100.0%
	9	93.3%	87.1%	93.8%	86.5%	100.0%	100.0%	100.0%
	11	86.4%	75.7%	86.7%	74.3%	100.0%	100.0%	100.0%
	13	81.0%	61.1%	81.3%	61.0%	100.0%	99.5%	100.0%
Optimum Pressure=9 bar	pH	EC $(\mu s/cm)$	EC $(\mu s/cm)$	TDS (mg/L)	TDS (mg/L)	C_{Fe} (mg/L)	C_{Fe} (mg/L)	C_{Zn} & C_{Mn} (mg/L)
	5	90.0%	83.6%	89.8%	83.8%	99.1%	99.1%	100.0%
	6.5	91.9%	83.7%	92.0%	83.7%	99.6%	99.3%	100.0%
	8	93.3%	87.1%	93.8%	86.5%	100.0%	100.0%	100.0%
	9.5	88.8%	85.9%	88.8%	85.1%	99.0%	100.0%	100.0%

3.2 Regression Model for RO

In order to have a better view on the influence of pH and pressure on removal rate of Fe and TDS (for COM influent), a regression model was proposed. In this model, α_0, α_1 and α_2 are constant coefficients and R_{Fe} stands for Fe removal rate. For all models, term of 'Sig.' means Significance F.

3.2.1 Fe Removal

Since Fe is the most frequent heavy metal existing in wastewater of steel making plant, a regression model is proposed in the following:

$R_{Fe}=\alpha_0+\alpha_1 pH+\alpha_2 Pressure$ *Eq. (3)*

Table 4 and Table 5 represent regression results and ANOVA details, respectively. For the overall regression, the coefficient of determination, R^2, equaled 0.651 (multiple R equals 0.810). It is evident that this regression was not ideal; however, it could predict the values of Fe removal to some extent because the Sig. value was around 0.07, which may seem a bit inappropriate, and the coefficient of regression was also acceptable. The standard error for this model was about 0.0025, and perhaps for one parameter, the p-value was not desirable but the model was mostly sufficient.

Table 4. Regression results for equation (3)

Coefficient	Value	Standard Error	P-value
α_0	0.979	0.007	4.61E-10
α_1	0.002	0.001	0.028
α_2	-1.66E-05	0.001	0.977

Table 5. ANOVA results for equation (3)

	df	*SS*	*MS*	*F*	*Sig.*
Regression	2.000	6.22E-05	3.11E-05	4.678	0.072
Residual	5.000	3.33E-05	6.66E-06		
Total	7.000	9.55E-05			

Table 6. Regression results for equation (4)

Coefficient	Value	Standard Error	P-value
α_0	1.249	0.117	0.000
α_1	0.001	0.011	0.989
α_2	-0.046	0.008	0.003

Table 7. ANOVA results for equation (4)

	df	*SS*	*MS*	*F*	*Sig.*
Regression	2.000	0.047	0.023	14.172	0.008
Residual	5.000	0.008	0.002		
Total	7.000	0.056			

3.2.2 TDS Removal

Likewise, a regression model is proposed for TDS rate of removal in the following:

$TDS=\alpha_0+\alpha_1 pH+\alpha_2 Pressure$ *Eq. (4)*

Table 6 and Table 7 represent regression results and ANOVA details, respectively. For this model, R^2 equals 0.850 (multiple R equals 0.921) which could mean a higher precision in comparison with R_{Fe}. The value of regression coefficient was very desirable here and 'Sig.' value was less than 0.05 which is completely satisfactory. At the same time, the P-value was probably not suitable for all parameters, but overall, it had an acceptable performance.

3.3 NF Membrane

Similarly, Table 8 shows the data related to nanofiltration membrane and removal efficiency of Fe, Zn, Mn, TDS and EC for both FE and COM influents.

Table 8. Removal efficiency of Fe, Mn, Zn, TDS and EC in NF membrane for different pHs and pressures

Type of Influent		WF	COM	WF	COM	WF	COM	COM
Constant pH=8	Pressure	EC $(\mu s/cm)$	EC $(\mu s/cm)$	TDS (mg/L)	TDS (mg/L)	C_{Fe} (mg/L)	C_{Fe} (mg/L)	C_{Zn} & C_{Mn} (mg/L)
	5	79.6%	82.9%	79.5%	83.3%	99.5%	100.0%	100.0%
	7	75.0%	79.8%	75.4%	80.0%	99.3%	100.0%	100.0%
	9	64.6%	67.7%	64.2%	67.5%	98.9%	98.4%	100.0%
	11	61.3%	61.8%	61.3%	61.3%	98.6%	97.9%	100.0%
Optimum Pressure=7 bar	pH	EC $(\mu s/cm)$	EC $(\mu s/cm)$	TDS (mg/L)	TDS (mg/L)	C_{Fe} (mg/L)	C_{Fe} (mg/L)	C_{Zn} & C_{Mn} (mg/L)
	5	70.9%	75.0%	70.6%	75.0%	99.2%	98.8%	100.0%
	6.5	68.8%	76.5%	69.1%	77.0%	99.1%	99.1%	100.0%
	8	75.0%	79.8%	75.4%	80.0%	99.3%	100.0%	100.0%
	9.5	73.0%	77.8%	72.8%	77.7%	99.6%	99.5%	100.0%

3.4 Regression Model for NF

3.4.1 Fe Removal

Since Fe is the most frequent heavy metal existing in wastewater of steel making plants, a regression model is proposed in the following:

$$R_{Fe} = \alpha_0 + \alpha_1 pH + \alpha_2 Pressure \qquad \text{Eq. (5)}$$

Table 9 and Table 10 represent regression results and ANOVA details, respectively. For the overall regression, the coefficient of determination, R^2, equaled 0.825 (multiple R equals 0.908). Although the p-value for α_1 was a little higher than 0.05, this regression model used for Fe removal rate could be acceptable. Meanwhile, the standard error for this model was 0.004.

Table 9. Regression results for equation (5)

Coefficient	Value	Standard Error	P-value
α_0	1.015	0.011	3.341E-09
α_1	0.002	0.001	0.143
α_2	-0.004	0.001	0.005

Table 10. ANOVA results for equation (5)

	df	*SS*	*MS*	*F*	*Sig.*
Regression	2.000	0.001	0.001	11.795	0.012
Residual	5.000	7.880E-05	1.577E-05		
Total	7.000	0.001			

3.4.2 TDS Removal

Likewise, a regression model is proposed for TDS rate of removal in the following:

$$TDS = \alpha_0 + \alpha_1 pH + \alpha_2 Pressure \qquad Eq. (6)$$

Table 11 and Table 12 represent regression results and ANOVA details, respectively. For this model, R^2 equaled 0.939 (multiple R equals to 0.969). The standard error for this model was also 0.021. This model was acceptable because the regression coefficient was above 0.90 which was an accurate value.

Table 11. Regression results for equation (6)

Coefficient	Value	Standard Error	P-value
α_0	1.085	0.067	1.000E-5
α_1	0.006	0.006	0.345
α_2	-0.040	0.005	0.001

Table 12. ANOVA results for equation (6)

	df	*SS*	*MS*	*F*	*Sig.*
Regression	2.000	0.035	0.017	39.042	0.001
Residual	5.000	0.002	0.001		
Total	7.000	0.037			

3.5 Flow Rates in RO and NF Membranes

Pure water flux was evaluated as a function of transmembrane pressure using Eq. (1). Figure 2 shows the permeate flux of RO and NF membrane versus applied pressure.

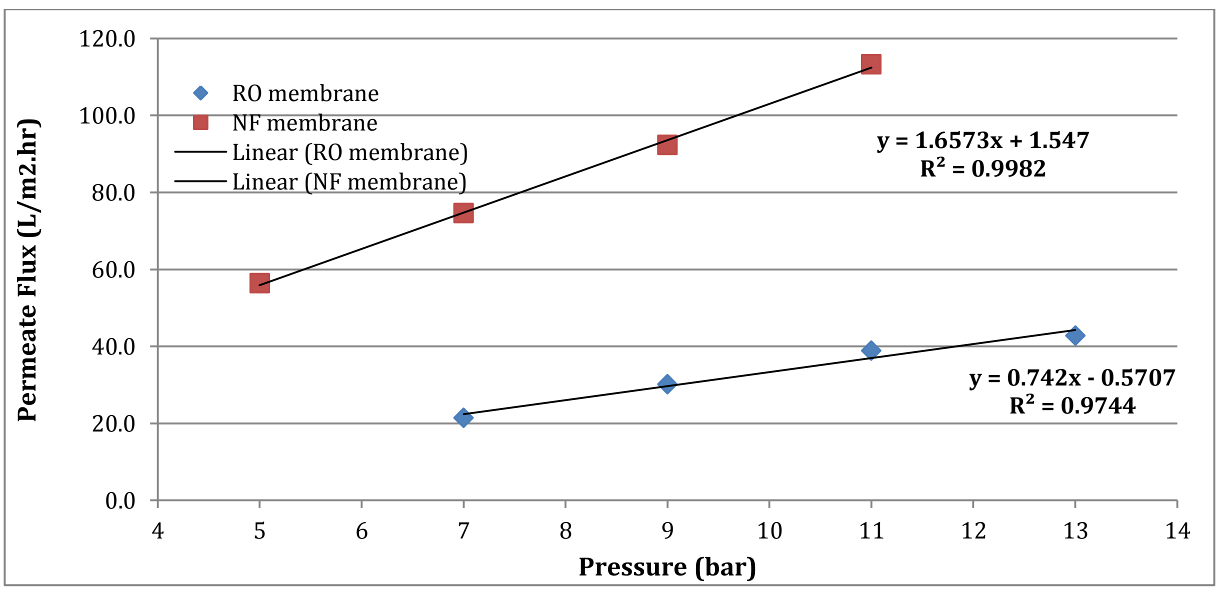

Figure 2. Pure water flux for RO and NF membranes in constant pH=8

3.6. Comparison of EC, TDS, C_{Fe}, C_{Zn} and C_{Mn} in RO and NF Membranes in Optimum Condition

Figure 3 shows the removal efficiency for the optimum pH and pressure values of RO and NF membranes (COM influent) to remove EC, TDS, Fe, Mn and Zn. As it can be understood from Figure 3, mostly the RO system depicts more acceptable performance, while the difference between RO and NF systems is usually negligible, especially in the optimum condition. As is seen in Figure 3, we can introduce nanofiltration as a successful method of treating wastewater as well as having better permeate flux value, which makes it economical and energy-saving due to lower applied pressure.

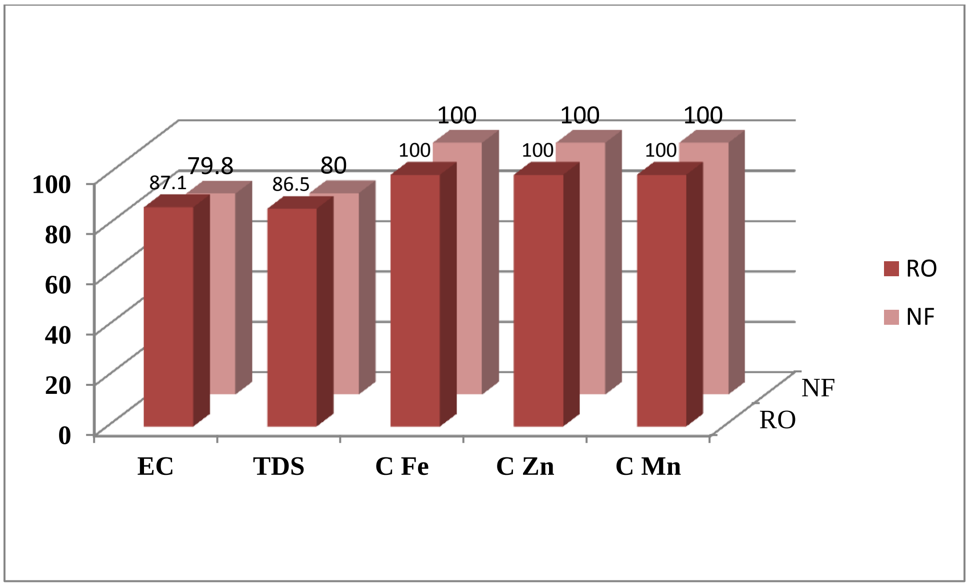

Figure 3. EC, TDS, C_{Fe}, C_{Mn} and C_{Zn} removal efficiency for RO and NF membranes

3.7. Effect of Higher Concentrations of Iron on Fe, Mn, Zn, TDS and EC Removal

As mentioned earlier, iron has the highest concentration among all present ions in the wastewater. In this part, concentration of iron varies from 23.3 mg/L to 35 mg/L then to 50 mg/L to show the ability of RO and NF membranes to treat this high amount of heavy metal from a wastewater. Table 13 shows the value of RO and NF membranes performance in higher concentrations of iron.

Table 13. Influence of high concentration on RO and NF performance

RO membrane	Con_{Fe} (mg/L)	$EC(\mu s/cm)$	$TDS(mg/L)$	C_{Fe} (mg/L)	C_{Mn} (mg/L)	C_{Zn} (mg/L)
	23.5	87.1 %	86.5 %	100 %	100 %	100 %
	35	85.1 %	84.4 %	99.7 %	100 %	100 %
	50	81.8 %	82.0 %	99.4 %	100 %	100 %
NF membrane	Con_{Fe} (mg/L)	$EC(\mu s/cm)$	$TDS(mg/L)$	C_{Fe} (mg/L)	C_{Mn} (mg/L)	C_{Zn} (mg/L)
	23.5	79.8 %	80.0 %	100 %	100 %	100 %
	35	73.9 %	73.8 %	99.6 %	100 %	100 %
	50	72.7 %	72.8 %	99.6 %	100 %	100 %

4. Discussion

As it can be seen from Table 3, the best results achieved at pressure equaled 9 bar. The highest possible Fe, Mn and Zn removal (100%) happened at this pressure, in addition to acceptable removal of EC and TDS (about 94%). According to this table, the removal efficiency for TDS, EC or Fe decreased from 9 bar to 11 bar, and also reduced from 11 bar to 13 bar which implied that concentration polarization had occurred and followed by convective transport (10). Optimum pH value equaled 8, as a result of which all parameters were removed favorably. Additionally, according to Table 3, it can be inferred that for RO membrane, WF influent had consistently higher removal efficiency in comparison with COM influent. In other words, when other ions and elements were added to WF influent, removal efficiency of iron, EC and TDS decreased, which indicated the interrupting interaction between different ions in RO membrane. This decrease in rejection can be explained in terms of the Donnan effect; negative anions present in the feed solution can easily pass through the membrane, and counter ions could also be forced to pass through the membrane to maintain electro-neutrality around the membrane, and in terms of osmotic pressure that increased due to the presence of other co-ions (10). Of course, because the reduction in removal efficiency between COM and WF influents was slight, it can be inferred that the concentration of the co-ions present in the influent was small, or their mobility was high. The main cause of this reduction can be attributed to the existence of elements such as Cu, Mn and Zn which might interrupt the iron removal or at least undermine the removal efficiency. In addition, it can be understood that EC and TDS removal had the same pattern in Table 3. As is illustrated in Table 8, the best results achieved in pressure equaled 5 bar, and pH equaled 8. At the same time, the pressure equaled 5 bar which could also rival 7 bar pressure, but due to higher water flux of pressure equaled 7 bar as the optimum pressure. The important achievement of NF membrane was the comparison between WF and COM influents, and the results of COM influents were more suitable than WF. In other words, when other elements and ions were added to WF influent, they excelled the removal efficiency of Fe, EC and TDS in general. This phenomenon can be attributed to the metal hydroxide precipitate and cake layer filtration in the NF membrane. This feature in the NF membrane can also be remarkable because even by adding other ions to the influent, not only the rejection does not change, but also it can improve the removal efficiency. As a general conclusion for both RO and NF membranes, the changes in rejection for all pressures and pHs were slight and even negligible. This can be attributed to the water permeation rate which is becoming greater at higher pressure, or to the solute diffusion rate which would not be expected to be affected significantly by higher pressure, because it is mainly controlled by the solute concentration (10).It should be noted that the presence of other cations increased the electric charge differences on the membrane side, though to gain the balance, more cations should cross the membrane. In this case, TDS and EC of permeate would increase. Since RO membranes exert the ion with 2 or 3 capacity, it was assumed that Na^{+} and $NH_4{}^{+}$ had passed the membrane, and as it is shown in Table 3 and Table 8, Zn^{2+} and Mn^{2+} were completely removed from wastewater, even when they had much greater concentration than other cations. As it can be inferred from Figure 2, while the applied pressure increased, the water flux also enhanced. It is notable that nanofiltration water flux was much higher (about 30% higher) than RO in the optimum conditions. From this point of view, NF is more economical. Al-Rashdi stated that as pressure increases, convective transport and concentration polarization become more important (10). According to Figure 2, change in the permeate flux versus pressure remains linear which indicates an insignificant concentration polarization (R^2 > 97%). In general, the change of flux with feed pH was very small, thus the data is not presented in this section, and as an overall result, for all pressure and pH values, the rejection value for Fe, Mn, Zn, TDS and EC are appropriate. Therefore, it can be said that even high pressures of RO and NF systems can also be pleasant. As it can be seen from Table 13, as the concentration of iron increases, EC and TDS removal in RO membrane decreases up to 6%, while the removal efficiency for Fe, Mn and Zn is almost in the same high possible amount. For NF membrane, TDS and EC removal efficiency decreases up to 9%, while again Fe, Mn and Zn removal efficiency is close to 100%. As a general conclusion, we can state that both RO and NF can tolerate the high concentration shocks of heavy metals even if TDS or EC removal decreases. Zhou introduced a model for membrane filtration (RO and NF) to estimate the total cost of the processes (14). In this section, according to their model, analytical estimation was made for both membrane filtration methods. The term (I) is related to pretreatment and reagent costs, which is not the objective of the current study. Term (II) is related to energy cost which should be analyzed (Eq.7).

$$F=I+II \quad I=[\sum_{i=1}^{n} K_i \frac{a_i}{1000}]Q \quad II=\frac{1}{3600}\frac{Q_f.P_f}{J_w.S}.C \qquad \textit{Eq. (7)}$$

'F' is the electricity charges required for a product per unit water (Yuan/lit), 'C' is electricity price (Yuan/KW.h), 'Q_f' is inflow water (lit/hr), 'P_f' is operating pressure (MPa), 'J_w' is the penetration flux (lit/m^2.hr), and 'S' is the effective surface of membrane (m^2).

$$\frac{F_{RO}}{F_{NF}} = \frac{(\frac{1}{3600}\frac{Q_f.P_f}{J_W.S}.C)_{RO}}{(\frac{1}{3600}\frac{Q_f.P_f}{J_W.S}.C)_{NF}} = \frac{1}{3600}\left[\frac{\frac{0.9\,MPa}{41}\times 30}{\frac{0.7\,MPa}{37}\times 30}\right] = \frac{0.66\,(\frac{Toman}{lit})}{0.57\,(\frac{Toman}{lit})} = 1.16$$

From the above equation, we can find that the price of RO membrane is 16% higher than NF. Of course, it should be noted that the initial price of NF membrane is almost 23% higher than RO system. But in the long-term approach, NF is more economic, which causes the initial cost of it to be neglected.

5. Conclusion

In the recent years, the necessity of saving water resources seems vital for all governments which makes researchers find new trends to treat wastewaters to produce demanded water at least for pollutant industries. As a general consequence, membrane filtration could have the following advantages: no need for chemicals (coagulation, flocculation, disinfectants, pH adjustment), good and constant quality of the treated water, process and plant compactness and simple operation. Steel making plants, as among the industries consuming high volumes of water to produce steel products, contain several heavy metals in their wastewater. The main objective of the present research was to introduce RO and NF system as a capable method to remove heavy metals (Fe, Mn and Zn), and decrease TDS and EC to favorable values. In the current study, the optimum pH and pressure were 8 and 9 bar, respectively, for the specific wastewater in RO method, while NF experienced pH and pressure levels of 8 and 7 bar, respectively, which are pleasant quantities. The interaction between ions and particles were also studied in the present study to show how different elements may interrupt the removal rate of iron. In addition, investigating the high concentrations of iron indicated that RO and NF have certain capabilities to treat high contaminated wastewater. As a general result, NF showed an acceptable performance with high water flow which made it more suitable for industries. At the end, the relative cost analysis showed that even if the initial price of NF is high, the energy consumption and total cost of RO will be higher.

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Conflict of interest

The authors would declare that no financial support was received from any specific organization to run this research.

Authors' contributions

AM has acted as thesis supervisor in this project. NB has run the experimental tests in the laboratory and he has helped to write the paper. SA has run the experimental tests in the laboratory PR has helped us to design tests to contribute in writing the paper. AY has done the modeling procedure in the paper as revised the paper for being scientifically correct.

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